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EFFECT OF Ca CONCENTRATION SUBSTITUTING FOR Ba ON STRUCTURE AND FERROELECTRIC PROPERTIES OF BZT-BCT MATERIAL

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ABSTRACT

In this paper, we report the effect of Ca substitution on the structure and ferroelectric properties of $BaZr_{0.2}Ti_{0.8}O_3$-$Ba_{1-x}Ca_xTiO_3$ (BZT-BCT). The BZT-BCT samples were synthesized by solid state reaction method. The X-ray results indicate that a phase structure competition appears in the Ca-substituted samples. Based on the hysteresis loops measured by Sawyer – Towermethod, we calculated the $\boldsymbol{E_c}$ and $\boldsymbol{P_r}$ values with the extreme value reaching 29.6 %. The ferroelectric properties of BZT-BCT materialstrongly depend on Ca concentration. The results may be related to a pinning effect concerning with the phase-structured competition in the material.

Keywords: BZT-BCT, substitution, ferroelectric, phase structure competition.

1. INTRODUCTION

Ferroelectric property in perovskite materials comes from the combination of the movements of atoms in cubic structure. In $BaTiO_3$ (BTO), spontaneous polarization (Ps) is induced by the deflection of Ti off the orthohedral of O site resulting the hybridization between Ti - 3d and O - 2p. The spontaneous displacement of Ba in BTO is so small because of the strong Ba-O bonding [1]. Inversely, in $PbTiO_3$, Pb-O bondings are the hybridization between the Pb-6s and the O-2p [1, 2].

Recently, the replacement of Ca for Ba in BTO has attracted many attentions due to its interesting properties, especially its piezoelectric property. The first report on $Ba_{1-x}Ca_xTiO_3$ (BCT) composite [3, 4] showed that the structure phase transition temperature T_{T-O}(tetragonal to orthorhombic) of BCT samples much reduces in dependence of Ca concentration while the Curie temperature $T_c$remains unchanged at 130 ^{0}C. The dependence of T_c and T_{T-O} on Ca concentration is quite different in case of Sr substitution for Ba in BTO. In the fact that, the decreasing in T_c and T_{T-O} in case of the Sr substitution was attributed to the ionic radius effect, the ionic radius of $Sr^{2+}$is smaller than that of Ba^{2+}[1, 2, 5]. In [6], Fu et al. has proved that

thetetragonal phase structure of BCT was stable when the Ca ions moved toward the direction [13]. In addition, the spontaneous polarization Ps in this structure exhibits a high value due to the displacement by Ca with smaller ion radius. $CaTiO_3$ (CTO) material was known as a paraelectric material with space group of Pbnm at 289 K. Ionic radius of Ca is relatively small, appropriated in the orthohedral TiO_6, and then no structure deformation in orthohedral TiO_6 caused by Ca andConsequently no ferroelectric polarization is formed. [7] Therefore, CTO materials exhibit no piezoelectric property although there is a large deformation in structure [8].

In this research, we studied in detail the effect of Ca substituting for Ba on structure and ferroelectric property of BZT-BCT system.

2. EXPERIMENTAL

$BaZr_{0.2}Ti_{0.8}O_3$-$Ba_{1-x}Ca_xTiO_3$ (BZT-BCTx) materials (for x = 28 %; 28.8 %; 29.2 %; 29.6 %; 30 % và 30.4 %) were fabricated by a solid reaction method. $BaCO_3$, $CaCO_3$, $ZrCO_3$ and TiO_2 with purity of 3N of Merck were used as starting materials. Powders of the starting materials were dried at 150^{o}C for 4h, then, weighed in amount to satisfy the stoichiometric ratio of the material.

The mixture of precursor powders was milled in alcohol for 24 hours by high energy ball milling and compressed into thin plate pellet with diameter of 10 mm and thickness of 1 mm. Samples were annealed at 1200 ^{o}C in air for 4 hours and sintered at 1450 ^{o}C for 4 hours. After heat treatment, Ag electrodes were made on the sample's sides and the samples were polarized under electric field of 25 kV/cm at room temperature.

Crystalline structure of materials was identified by using a X-ray Diffractometer D5000-SIEMENS equipped with $Cu_{K\alpha}$ radiation (λ = 1.5406Å). The XRD parttens of the material's powder samples were reccorded at room temperature. Ferroelectric hysteresis was measured by Sawyer – Tower method using oscilloscope TDS 1012B (Tektronix).

3. RESULTS AND DISCUSSION

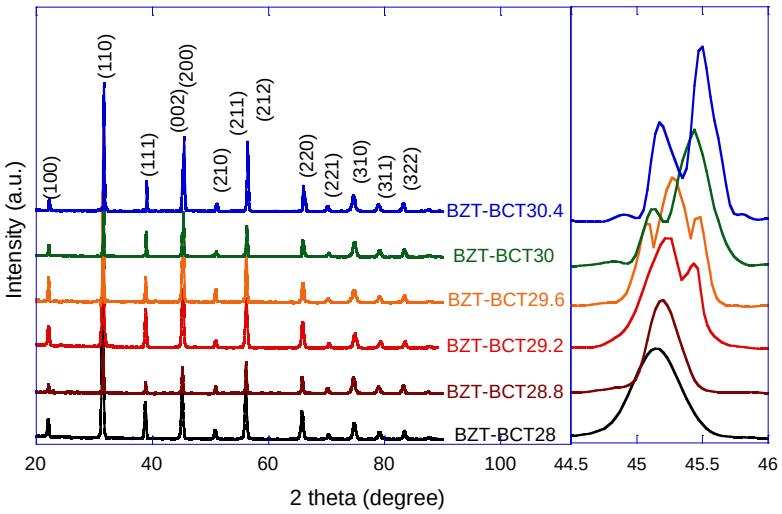

Figure 1. XRD pattern of BZT-BCTx.

Figure 1 shows the XRD patterns of BZT-BCTx samples. The samples with concentration x of smaller than 29.6 % (corresponding to Ba/Ca ratio is 85.2/14.8) have pure phase of BZT-BCTx; the samples with concentration x of larger than 30 %, appear a new peak of the $CaTiO_3$ component.

Table 1. Crystalline parameters of BZT-BCT.

SAMPLES	*A* (Å)	*B* (Å)	*C* (Å)	α (°)	β (°)	γ (°)
BZT-BCT28	4,0060	4,0060	4,0060	89,9181	89,9181	89,9181
BZT-BCT28.8	4,0061	4,0061	4,0061	89,9141	89,9141	89,9141
BZT-BCT29.2	4,0062	4,0062	4,0068	90,0000	90,0000	90,0000
BZT-BCT29.6	4,0064	4,0064	4,0079	90,0000	90,0000	90,0000
BZT-BCT30	4,0049	4,0049	4,0082	90,0000	90,0000	90,0000
BZT-BCT30.4	4,0036	4,0036	4,0075	90,0000	90,0000	90,0000

As can be seen, the diffraction peaks shifted to higher angle when Ca-substituted content increased, and some diffraction peaks became divided into several peaks, for instance the peak at 2θ of 44.7°. Especially, when Ca concentration reached to 29.6 %, the peaks at 2θ of 44.7° became separated into three peaks corresponding to three structures of cubic, tetragonal, and orthogonal. When x is higher than 30 %, they have tendency to incorporate into 2 peaks corresponding to tetragonal - orthogonal structures. The unique of this structure can be resulted in the critical points of $\boldsymbol{E_c}$ and $\boldsymbol{P_r}$ at x of 29.6 %. The detailed crystalline parameters were listed in Table 1. The obtained results show that BZT-BCT material presents orthorhombic structure assigned as characteristic structure of BZT at x below 29.2 % while it offers tetragonal structure of BCT. Interestingly, orthorhombic structure and tetragonal structure simultaneously appeared in BZT-BCT material at x= 29.6. This was confirmed through the separation of XRD peak observed at $2\theta = 44.7^0$ and well fitting result of XRD peaks to Gauss function as shown in Fig. 2. It can be seen that at y = 29.6, tetragonal structure was characterized by peaks of $(002)_T$, $(200)_T$ responding to 2 theta of 45.21°và 45.42° and orthorhombic structure was assigned with peak of $(002)_R$ corresponding to 2 theta of 45.37°). According to W. Wersing, W. Heywang et al. [9], the component ratio of tetragonal structure was estimated by the following formula:

$$F_T = \frac{I_T^{200} + I_T^{002}}{I_T^{200} + I_R^{200} + I_T^{002}}, \quad (1)$$

in which: $I_T^{200}, I_T^{002}, I_R^{200}$ are intensity of peaks at (200), (002) corresponding to tetragonal and orthorhombic, respectively. In the case of BZT-BCT29.6, the ratio of tetragonal structure to orthorhombic structurewas determined to be of around 69 %.

At room temperature, BZT-BCTx with x = 0 has ferroelectric rhombohedral structureas reported by Devries and Roy [10]. Structure of BZT-BCTx at room temperature was modified from orthorhombic (O) to tetragonal (T) and phase transition temperature T_C increased with the increasing of Ca content.

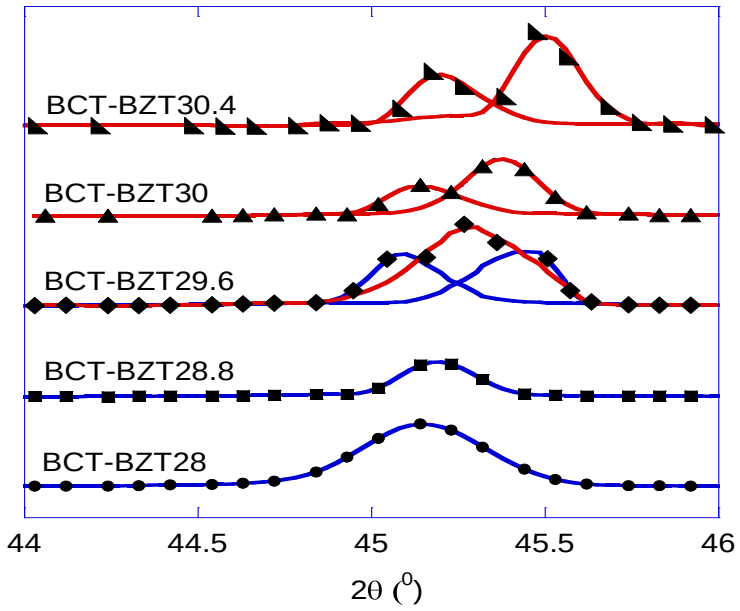

Figure 2. XRD pattern of BZT-BCT with 2 theta in range from 44^o to 46^o (symbol) and the fitting curves to the Gauss function (line).

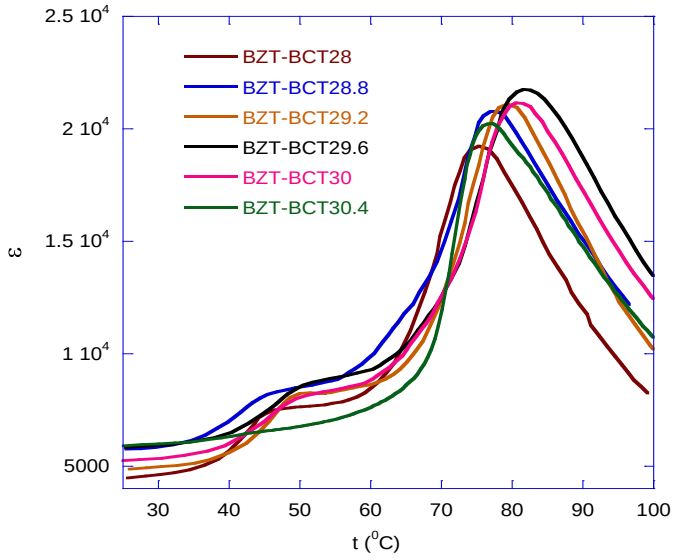

Figure 3. The temperature dependence of dielectricity of BZT-BCTx.

To understand the influence of temperature on the structure of BZT-BCTx materials, the dielectric-constants measurements were carried out in temperature range of 20 ^{o}C – 100 ^{o}C as shown in Figure 2. Similarly to recently reports [11, 12, 13], in case of x = 0, it is not easy to distinguish three phase transition processes in BZT-BCT. However, C-T, T-O and O-R transitions in $BaTiO_3$ were observed in the dielectric permittivity curves versus temperature as shown in Fig. 2. The O-T and T-R temperature transitions can be estimated from the peak points in the dependence of dielectric constant. It was found that a shift of the O-T and T-R temperature toward lower temperature when Ca concentration decreased. Besides, Ca

concentration has affected on the stability of ferroelectric property of tetragonal phase. The Currie temperature and other ferroelectric propertiesof the material are related with the change of unit cell volume. This result can be related with the deflection of Ca off-centering which plays an important role in modifying the polarity state of BZT-BCTx.

Table 2. The transition temperature depending on Ca content.

Sample	BZT-BCT28	BZT-BCT28.8	BZT-BCT29.2	BZT-BCT29.6	BZT-BCT30	BZT-BCT30.4
T_{T-O} (^{0}C)	75	77	79	82	80	76
T_{T-R} (^{0}C)	45	46	49	51	48	x

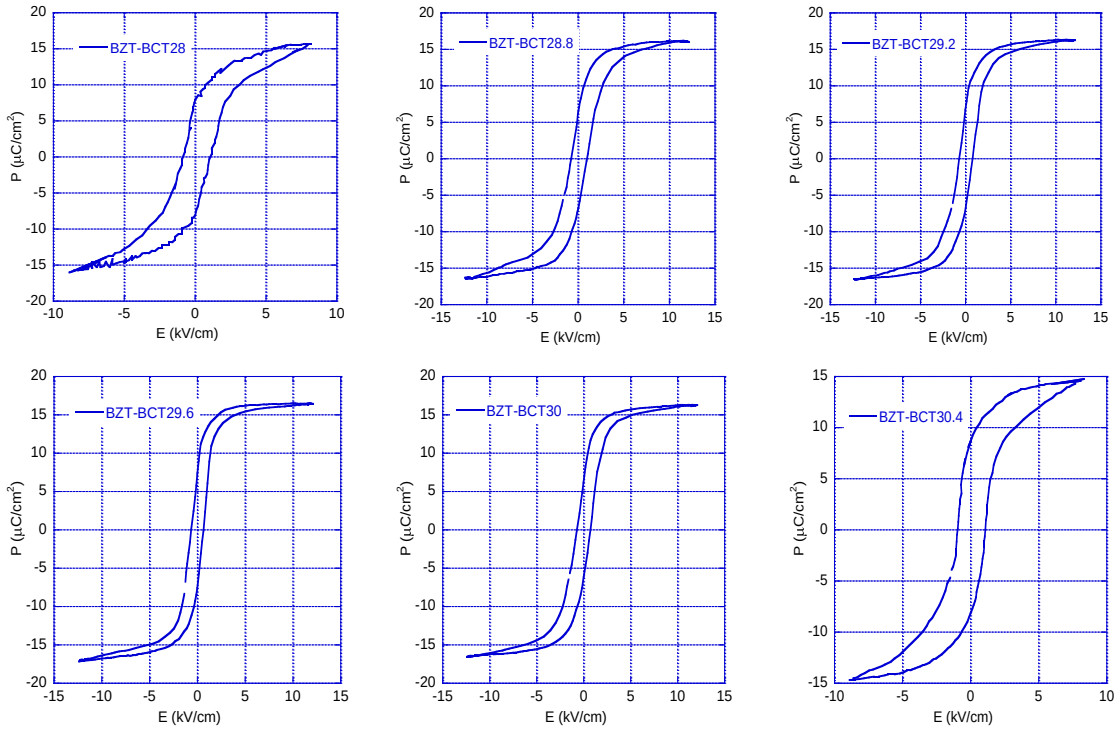

Figure 4. Electric hysteresis curves of samples.

Figure 4 shows the electric hysteresis curves of all samples measured by S-T method. From hysteresis curves, the E_C and P_r were estimated for all samples with the value were listed in Table 3. The samples have small Ec that confirm soft ferroelectric property of the prepared material. It is interesting that the E_C decrease first when Ca content increase from 28 % to 29.6 % and increase after that in dependence of Ca concentration over 29.6 %. In contrast, the P_r increases with the increasing of Ca content to 29.6 % and decrease after that with increasing the Ca content over 29.6 %. This could be explained as following: ferroelectric properties of BCT not only was contributed by the mobility of Ti^{4+}, but also by the mobility of Ca^{2+} ions exited in BCT material.

Table 3. E_c and P_r values depends on the concentration x.

Samble	BZT-BCT28	BZT-BCT28.8	BZT-BCT29.2	BZT-BCT29.6	BZT-BCT30	BZT-BCT30.4
E_c(kV/cm)	1,07	1,01	0,79	0,64	0,72	1,08
P_r($\mu C/cm^2$)	8,6	8,66	8,75	8,77	8,33	8,25

It is suggested that the dependence of of $\boldsymbol{E_c}$, $\boldsymbol{P_r}$ on Ca content in BZT-BCTx is due to the difference of ionic radius of Ca^{2+} and Ba^{2+}. Ca^{2+} ions with smaller ionic radius are more flexible that effectively contribute to polarization processes, which results in the changing of the spontaneous polarization. According to Goldschmidt [14], when Ca concentration increases, the crystalline symmetry of BZT-BCTx structure reduces and the crystalline structure is deformed that change its tolerance parameter as follows:

$$t = \frac{(r_A + r_O)}{(r_B + r_O)\sqrt{2}} \qquad (2)$$

where, r_A, r_B and r_O respectively are ionic radius of ion at A, B and O positions. Values of radii here depend on structure and their coordination number.

In the case of t = 1, the cations which occupy at A and B sites have the similar radius as anion O. In case of t < 1, cations at B positions are larger compared to their spaces then lattice constants are changed while cations at A positions can move. When t >1, the processes are reversed.

Using formula (2), we calculated the tolerance in case of without Ca, *t = 0.78*, and in case of Ca completely substituted for Ba, t = 0.68 (with ionic radius of ions respectively are $r_{Ca^{2+}} = 0.134nm; r_{Ba^{2+}} = 0.156nm; r_{Ti^{4+}} = 0.19nm; r_{O^{2-}} = 0.06nm$ [15].

Ca^{2+} ions can leave to the positive charge center and then the negative charge center deflected that induce spontaneous polarization, hence, material has ferroelectric or anti-ferroelectric properties. The minimum and maximum values of $\boldsymbol{E_c}$ and $\boldsymbol{P_r}$ at x = 29.6 % is related with the structural phase competition in material at this concentration. Therefore, the spontaneous polarizations undergo the highest effect of structural phases, causing the critical values of $\boldsymbol{E_c}$ and $\boldsymbol{P_r}$.

4. CONCLUSION

We successfully fabricated high quality BZT-BCTx material with different Ca-subtituted content. X-ray diffraction spectra of samples showed the change in structure of composite when Ba ions were substituted by Ba. There was a split in peak at $2\theta = 44.7^o$. The dependence of dielectric constant on temperature with different Ca concentrations allowed us to determine the O-T and T-C transition temperatures. Ca concentration has influenced on the stability of ferroelectric property in O and R structure of the material. The critical values of Ec and Pr at Ca concentration of 29.6 % is related with a competition of the structure phases in the material.

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